

## RESIDUAL STRESS IN PZT THIN FILMS AND ITS EFFECT ON FERROELECTRIC PROPERTIES

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## ABSTRACT

The residual stress in solution derived  $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ , PZT 53/47, films was determined by measuring the bending of the substrate due to the stress. The substrate consisted of an oxidized (100) silicon wafer with 300 nm coating of platinum. In all cases the stress was tensile. Films fired at a temperature in the range where pyrochlore formation occurs (500° to 575°C) had the highest residual stresses, 200 to 350 MPa, whereas those fired at higher temperatures, 600° to 650°C, where the perovskite phase forms had stresses of 100 to 200 MPa. Stress measurements made during film firing indicate that the pyrochlore containing films had higher residual stress because their coefficient of thermal expansion was much larger than that of predominantly perovskite films. The effect of the amount of stress on ferroelectric properties was studied by making measurements on a film with and without the application of an external stress. The external stress was applied by bending a circular section of the substrate, which effectively lowered the amount of tensile stress in the film by ~30%. Decreasing the stress in this manner was found to increase the remanent polarization by ~11% and the dielectric constant by ~2%.

## INTRODUCTION

When a thin film is fabricated on a substrate, the film is mechanically constrained by the substrate. Therefore, any free strain that the film would otherwise undergo during processing results instead in the development of stress in the film. Processes such as thermal expansion and phase changes produce free strain, and thus stress in a constrained film. Accordingly, residual stresses of several hundred MPa are not uncommon in thin films. A chemically prepared PZT thin film on a silicon substrate would therefore be expected to have appreciable residual stress due to the thermal expansion mismatch between the film, whose coefficient of thermal expansion changes during thermal processing, and silicon and since crystallization to the higher density perovskite phase occurs during thermal processing.

Since PZT films are being developed for electrical applications, such as non-volatile memory devices, the effects of residual stress on the dielectric and ferroelectric properties of the film must be determined. Stress can influence these properties in a variety of ways. For example, the composition of the morphotropic phase boundary and the Curie temperature are altered by the presence of stress.[1,2] Also, since PZT is ferroelastic, stress can change its domain structure.[3-5] In this study, the amount of residual stress in chemically prepared PZT thin films was determined. The origin the residual stress and the effect of stress on ferroelectric properties were studied.

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## EXPERIMENTAL PROCEDURE

Film Fabrication

PZT thin films were fabricated using a solution deposition technique based on the work of Sayer and co-workers.[6,7] In this process, lead acetate trihydrate was dissolved in excess acetic acid and then dehydrated by heating to 105°C. Zirconium butoxide-butanol and then titanium isopropoxide were added to the lead acetate solution. A variation of this process in which the three precursors were added in the opposite order and in which lead (IV) acetate was used instead of lead acetate trihydrate was used to make some of the films and will be referred to as the inverted mixing order process.[8] The composition of all films was PZT 53:47 with 5 mole excess Pb. Films were deposited by spin-casting at 3000 rpm for 50 s. Films were heat treated at 300° to 350°C for 5 min after each layer was deposited. Final films consisted of four layers and were approximately 0.4  $\mu$ m thick.

For measurement of stress in the PZT films, 75  $\mu$ m thick 2 inch diameter silicon (100) wafers were used. The wafers were first oxidized by heating at 1200°C in O<sub>2</sub> for 1 hr. For the room temperature stress measurements, the bottom electrode consisted of 300 nm of platinum on top of 50 nm of titanium, both formed by sputtering. For reasons discussed below, no titanium layer was used in the bottom electrode for the samples used to measure the stress in the PZT during heating. Films for the experiments to determine the effect of stress on ferroelectric properties were made on 0.5 mm thick 3 inch diameter silicon (100) wafers which had a 400 nm thick CVD SiO<sub>2</sub> layer and a two layer, titanium-platinum electrode deposited on them.

Residual Stress at Room Temperature

The residual stress in the PZT films made by the process of Sayer and co-workers was determined by measuring the parabolic deflection of the wafer substrate due to the stress in the film. The stress,  $\sigma$ , in a film of thickness  $t$  is related to the amount of deflection,  $\delta$ , that a substrate of length  $L$  and thickness  $d$  undergoes by:[9]

$$\sigma = (4\delta/3t) (d/L)^2 (E/(1-\nu)) \quad (1)$$

where  $E$  is the Young's modulus and  $\nu$  the Poisson's ratio of the substrate (silicon) in the direction that  $L$  is measured. For a material such as silicon that is cubic, the quantity  $E/(1-\nu)$  is a constant for any direction in the (100) plane. For silicon this constant is equal to  $1.8 \times 10^{10}$  Pa.[10]

The amount of deflection was determined using a profilometer (Dektak IIA, Veeco Instruments). The sample was supported at three points and its profile measured over a length of 5 to 10 mm. A very small stylus load was used so that the deflection was not changed by the load of the stylus. That the load of the stylus or the weight of the substrate itself did not contribute to the deflection was confirmed by verifying that profiling both surfaces of the wafer gave a deflection of the same magnitude. The deflection due to the PZT film was determined by measuring the deflection of a length of the substrate both with the film present and after it had been etched off, and then subtracting the latter from the former. The thickness of the PZT films were also determined with the profilometer. Deflection and thickness measurements were made on samples heated for 30 min at temperatures from 500° to 650°C and then were used to calculate the residual stress.

### Stress During Heating

The stress in the film was determined as a function of temperature during thermal processing by measuring the substrate deflection at temperature. This was accomplished by using the laser reflectance technique.[11] In this technique, two initially parallel He-Ne laser beams reflect off the sample inside a furnace and are then directed to a screen several meters away so that their separation can be measured. The deflection can then be calculated from the initial and final beam separations and the distance that the beams travel from the sample to the screen, noting whether or not the beams intersect before reaching the screen.

To calculate the stress in the PZT, the deflection due to the PZT must be determined. The deflection due to the PZT film must be determined by subtracting the deflection due to the stress in the electrode from the total deflection. The deflection due to the electrode must be measured by heating a sample that is identical to the original sample except that the PZT has been removed. Initially, this was attempted by measuring the deflection during heating of a wafer with a Ti-Pt electrode and a PZT-film, made by the process of Sayer and co-workers, and then measuring the deflection during the same heating schedule for an identical sample from which the PZT had been etched off. However, the deflection due to the bottom Pt-Ti electrode during heating was found to depend on whether or not the PZT film was present on top of it. Therefore, bottom electrodes without any Ti layer were used in these experiments since they behaved the same with or without the PZT film. The heating schedule used consisted of a ramp rate of 5°C/min with 3 min holds every 50°C to measure the beam separation and a 30 min hold at the maximum temperature, 575° or 675°C. The thickness of the film at each of the hold temperatures was measured by heating other pieces of the same wafer to each of the hold temperatures, cooling and measuring the film thickness of each sample with the profilometer. Stress was calculated using the elastic properties of silicon at each temperature.[12]

### Effect of Applied Stress on Ferroelectric Properties

To determine if the amount of stress in a PZT film affects its ferroelectric properties, electrical measurements were made on a film with and without the application of an external stress. Use of the same film ensured that other factors such as phase composition and grain size were the same when measurements were made with different amounts of total stress. The external stress was applied by flexing a circular section of a 0.5 mm thick wafer by applying a uniform load across it. This was done by placing the wafer, PZT side up, on a 3.4 cm diameter teflon o-ring which rested on a flat plate with a small hole in its center, and then pulling a vacuum through the hole. This caused a biaxial compressive stress in the PZT film above the center of the o-ring, where the electrical properties were measured, that added to the residual stress.

The calculation of the magnitude of the stress in the PZT due to the pressure difference is not as straightforward as might be expected.[13] One reason for this difficulty is that the analyses which have been done on this problem all assume that the wafer has isotropic elastic properties, which, of course, single crystal silicon does not have. Another problem is that as the load applied to the wafer increases, the membrane stretching stress becomes increasingly large relative to the bending stress. The membrane stress is always tensile and uniform across the wafer cross section and is negligible for low loads. The bending stress varies linearly across the wafer cross section from compressive at the top surface to tensile at the bottom. This

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behavior gives rise to a maximum in the magnitude of the compressive stress at the top surface at the center of the deflected portion of the wafer at some value of applied load. Therefore, to approximate the stress at the top surface in the middle of the wafer, an approximate equation was used along with average values of  $E$  and  $\nu$  for (100) silicon.[10,13] The equation used was for a simply supported wafer with an immovable edge, since the edge was constrained by the portion of the wafer outside of the deformed region. For the geometry of wafer and o-ring used, this equation predicts that the stress is about 75 MPa for the pressure difference used (640 torr).

The magnitude of the compressive stress in the PZT film at the center of the deflected region of the wafer can be related to that in the silicon by assuming that their strains are equal:

$$\sigma_{PZT} = (E_{PZT}/E_{Si})((1-\nu_{Si})/(1-\nu_{PZT})) \sigma_{Si} \quad (2)$$

When values are substituted for the elastic properties, equation 2 becomes  $\sigma_{PZT} = 0.4 \sigma_{Si}$ , or about 30 MPa.[9,13] The film used in these experiments was made by the inverted mixing order process and was heated to 650°C for 0.5 hr. The residual tensile was determined on a film processed identically except on a 75  $\mu$ m thick wafer. The magnitude of the stress was -100 MPa. Therefore, the external stress lowered the tensile stress by about 30%.

The dielectric and ferroelectric properties of this sample were then measured with and without the external stress. The dielectric properties were measured with a Hewlett Packard 4194A impedance analyzer with a 1 V 100 kHz signal. Hysteresis loops were obtained with a Radiant Technologies RT 66 A ferroelectric test system in the virtual ground mode.

## RESULTS AND DISCUSSION

### Residual Stress at Room Temperature

The residual room temperature tensile stress in PZT films from two different batches of precursor solutions which had been fired at various temperatures are shown in Figure 1. For both films, the initial residual stress after the 350°C pyrolysis heat treatment was about 200 MPa. This stress is caused by the constrained drying and pyrolysis that occur due to the presence of the substrate. When the films were heated to 500° or 550°C, the stress increased. Other studies have shown that the pyrochlore phase crystallizes in these films in this temperature range.[7] X-ray diffraction of one film fired at 550°C confirmed that pyrochlore was present. On the other hand, when the films were fired at higher temperature, 600° to 650°C, where x-ray diffraction indicated that the perovskite phase was predominant, the residual stress was considerably lower, 100 to 150 MPa. Although the two different films behaved similarly, the films from solution A had higher stress when fired at 550°C and lower stress when fired at higher temperatures. This indicates that the films from this solution crystallized more fully to either of the crystalline phases than did those from the other solution, due to some undetermined minor variation in the solution preparation. To understand why the phase composition of the film strongly influences the residual stress, stress in the films was determined in-situ during the heat treatment.

### Stress During Heating

The tensile stress in PZT films during heating is shown for films heated to two different maximum temperatures in Figure 2. During initial heating, the stress decreases gradually, indicating that the thermal expansion coefficient of the amorphous PZT film is larger than that of silicon. Between 475° and 525°, the stress starts to decrease faster with temperature, indicating formation of a higher thermal expansion coefficient phase, pyrochlore. Stress further decreases during the hold at 575°C, indicating continued formation of the low density pyrochlore phase. For the film heated to 675°C, the stress increases from 575°C to 675°C, most likely due to the formation of the higher density perovskite phase that occurs in this temperature range. During cooling of the film heated to 575°C, the stress increases sharply, indicating that the thermal expansion coefficient of the pyrochlore, the predominant phase in the film, is very much higher than that of silicon. When the film heated to 675°C is cooled, the stress increases until the Curie temperature (near 400°C). Upon further cooling, the stress decreases, indicating that the thermal expansion coefficient of the film is less than that of silicon, in agreement with published thermal expansion data for perovskite PZT 53:47 and (100) silicon.[14,15] These results indicate that the reason the residual stress at room temperature depends on the phase composition is that the thermal contraction of pyrochlore is much larger than that of perovskite.

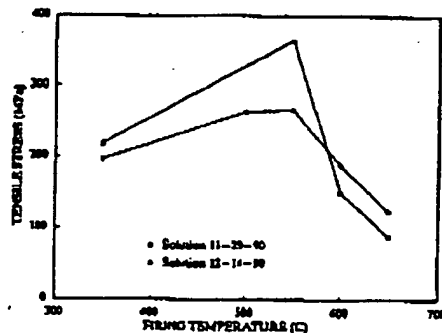


Figure 1. The dependence on firing temperature of residual tensile stress in PZT films.

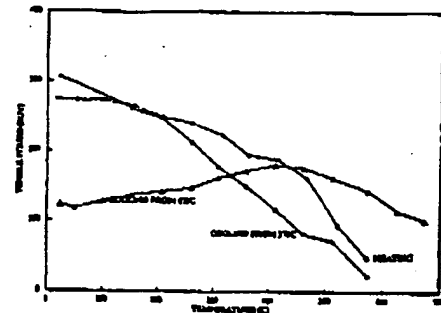


Figure 2. The stress in PZT films during firing.

### Effect of Applied Stress on Ferroelectric Properties

Repeated measurement of the capacitance at the center of the deformed region with and without application of the external stress indicated that the dielectric constant increased reversibly by ~2% when the external stress was applied. Similarly, the hysteresis loops taken with a maximum voltage of 7 volts on the same electrode dot with and without the external stress indicated that the remanent polarization increased reversibly when the stress was applied from about 26 to 28.9  $\mu\text{C}/\text{cm}^2$ , an 11% increase. The coercive field also increased slightly, ~1.5% when the external stress was applied. Although relatively small, these changes were produced by only a 30% decrease in the stress so that more significant changes would occur if these trends continued with further decrease in stress.

The changes in dielectric constant and remanent polarization do not seem to be caused by domain switching for several reasons. First, since the dielectric constant is lowest in the direction of the polarization vector, domain switching due to the external compressive stress, which would tend to

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cause the domains to switch so that the polar axes are as perpendicular to the plane of the film as possible, should cause the dielectric constant to decrease. The fact that the change in these properties was reversible upon removal of the stress also weighs against domain switching.[3,4] Therefore, it appears that the changes must be due to changes in the properties of the domains due to the deformation of the unit cell produced by the stress, similar to what has been observed for  $\text{BaTiO}_3$ . [16] This occurs because in a film with randomly oriented domains, 2/3 of the polar axes are more closely parallel to the plane of the film than perpendicular to it. Therefore, the applied compressive stress tends to make the unit cell more cubic, thus increasing its dielectric constant. Also, the applied stress increases the anisotropy of the unit cell along the polar axes, and thus the magnitude of the polarization, for those domains that have their polar axes nearly perpendicular to the plane of the film, the ones that contribute the most to the remanent polarization.

#### CONCLUSIONS

The magnitude of the residual tensile stress in solution derived PZT films is primarily determined by the amounts of the pyrochlore and perovskite phases present. Because of its higher coefficient of thermal expansion, the pyrochlore phase causes a higher residual stress than does the perovskite. Moreover, changing the amount of stress in the PZT film by applying an external stress directly affects the electrical properties of the film. The remanent polarization increased by -11% and the dielectric constant increased by -2% when the stress in the film was decreased by -30%. This suggests that production of PZT films by a process that produces low residual tensile stress, or possibly a residual compressive stress, could potentially produce films with superior properties. However, in that case the stress will also be different during cooling from the firing temperature so that the domain structure of the film could also be different, thus producing other effects on the film's properties.

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